Solid-State CPMAS ^{13}C NMR and Pyrolysis-GC-MS Studies of Coal Structure and Liquefaction Reactions

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Abstract

The objective of this work is to delineate the chemical reactions during liquefaction of low rank coal by characterizing the resultant structural changes in coal macromolecular network, using cross-polarization magic angle spinning (CPMAS) solid-state ^{13}C NMR and flash pyrolysis-GC-MS (Py-GC-MS). We analyzed the THF-insoluble residues from liquefaction of a Montana subbituminous coal at different final temperatures ranging from 300 to 425°C in three different solvents under temperature-programmed (TPL) and non-programmed (N-PL) conditions. The combined use of CPMAS ^{13}C NMR and Py-GC-MS on the residues from TPL revealed a progressive loss of oxygen-containing species, and the gradual loss of aliphatic-rich species from the coal macromolecular network with increasing temperature from 300 to 425°C. The higher efficiency of TPL in the presence of H-donor, compared with conventional runs, is closely associated with H-transfer from tetralin to reactive species and removal of specific oxygen functional groups such as carboxyl and catechol groups from the coal during the programmed heat-up. Loss of these specific functional groups in early stage of TPL probably moderates or minimizes the occurence of retrogressive reactions, thus increasing the conversion.

Introduction

Modern solid state nuclear magnetic reasonance (NMR) spectroscopy originated in 1970s when cross-polarization (CP) and magic angle spining (MAS) techniques were developed and combined (CPMAS) [1-3]. Since the first paper on NMR of coals was published by Vander Hart and Retcofsky in 1976 [4], solid-state NMR has been applied extensively in characterization of coals. The techniques of CPMAS and dipolar dephasing MAS (DDMAS) ^{13}C NMR can provide useful structural information on insoluble organic solids. In recent years, solid-state NMR has rapidly become one of the most important non-destructive techniques for studying the structure of solid coal, coal macerals, coal-derived products, geochemical samples, and other organic solids [5-12]. Flash pyrolysis-gas chromatography -mass spectrometry (Py-GC-MS) is also an important analytical technique for structural study of polymeric materials [13-16]. Py-GC-MS is relatively simple in theory, and can be viewed as a combination of the well known MS techniques with pyrolysis-GC [17,18]. While these techniques have been applied in many investigations, very few applications have been made in coal liquefaction studies.

The present work is a part of our research on temperature-programmed liquefaction of low rank coals, and involves the spectroscopic study of coal structure and liquefaction reactions using the combination of CPMAS ^{13}C NMR and Py-GC-MS [19-21]. The NMR technique has an advantage of providing the information related to the type and distribution of aromatic and aliphatic carbons in a non-destructive and quantitative fashion. Its disadvantage is that the information from NMR does not provide a direct picture of the molecular components and their environments. This is partly because the coal organic matrix is a complex mixture, whose individual components can not be resolved by NMR. Py-GC-MS is a very useful technique for studying the molecular components or structural units of polymeric organic solids. Py-GC-MS is also a fingerprinting technique [16]. However, the major drawback to Py-GC-MS is that the proportion of coal that can be volatilized and analyzed by GC-MS is relatively small. For many coals more than half of the organic material remains as a residue. Since each technique has advantages and disadvantages, we can make complementary use of these techniques by using them in tandem. The combined use of solid state NMR and Py-GC-MS has the potential to provide both average structural information and specific molecular components, and when applied to properly selected samples, can provide insights into the major and minor changes in coal structures and structural transformations involved in coal liquefaction processes [19,20].

Experimental

The coal used was a Montana subbituminous coal obtained from the Penn State Coal Sample Bank (DECS-9 or PSOC-1546). The characteristics of this coal are as follows: 33.5% volatile matter, 37.1% fixed carbon, 4.8% ash, 24.6% moisture, on a raw coal basis; 76.1% C, 5.1% H, 0.9% N, 0.3% organic S, and 17.5% O, on a dmmf basis. The coal was dried in a vacuum oven at 95°C for 2 h before use. The vehicle used was tetralin, a known H-donor. Liquefaction was carried out in 25 ml microautoclaves using 4 g coal (< 60 mesh) and 4 g tetralin under 6.9 MPa H_2. After the reaction, the liquid and solid products were separated by sequential extraction with hexane, toluene and THF.

The THF-insoluble residues were analyzed by solid state ^{13}C NMR and Py-GC-MS. Our preliminary tests showed that a trace amount of THF remains in the residue even after vacuum drying at 100 °C for over 6 h, which significantly interferes with the spectroscopic characterization using CPMAS ^{13}C NMR and Py-GC-MS. Therefore, prior to analyses, all the THF-insoluble residues were washed first by using actone and then n-pentane, followed by vacuum drying at 100°C for 6 h. This procedure was found to be very effective for removing trace amount of THF.

The NMR spectra were acquired on a Chemagnetics M-100 NMR spectrometer by using the combined high power proton decoupling, cross-polarization and magic-angle-spinning (CPMAS) techniques. The measurements were carried out at a carbon frequency of 25.1 MHz. About 0.4-0.6 g of a sample was packed in a bullet-type Kel-F rotor (0.4 ml capacity); the spining speed of the rotor was about 3.5 kHz. The experimental conditions for all the samples are as follows: a cross-polarization contact time of 1 ms and a pulse delay time of 1 s. An instrumental calibration test was performed with the rotor containing hexamethylbenzene, which was adjusted to the magic angle (54.7°) to give the correct chemical shifts. To assure good spectra with high signal-to-noise ratios, the number of pulses accumulated for obtaining a spectrum was at least 10,000, and most of the spectra were obtained with numbers of scans between 20,000 to 35,000.

Py-GC-MS analysis was performed on a Du Pont 490B GC-MS system fitted with a 30 m x 0.25 mm i.d. capillary column DB-17 coated with 50% phenylmethylsilicone stationary phase with a film thickness of 0.25 um, and interfaced to a Chemical Data Systems Pyroprobe-1000 pyrolyzer. Helium was used as a carrier gas. The data acquisition and data processing were controlled through a computer-aided system. Prior to the start of data acquisition, the samples were flash-pyrolyzed at 610°C for 10 seconds, during which the pyrolysates (pyrolysis products) were retained in the clsoe-to-inlet part of the capillary column by colling with liquid nitrogen. The column was held at 40°C for 5 minutes and subsequently programmed to 280°C at a rate of 4°C/min. The mass spectrometer was operated in the electron impact mode at 70 eV. In order to derive information related to the macromolecular network, the low molecular species in the coal and coal liquefaction products were removed by THF extraction prior to Py-GC-MS analysis. The other experimental details about the NMR and Py-GC-MS are similar to those described elsewhere [7].

Results and Discussion

Characterization of DECS-9 Subbituminous Coal

Because the liquefaction residues are THF-insoluble, it was necessary to obtain a corresponding baseline spectrum with the THF-insoluble residual part of the raw coal. Figure 1 shows the CPMAS ^{13}C NMR spectra of the fresh DECS-9 coal and the unreacted but THF-extracted DECS-9 coal. It is interesting to note that the THF-extracted coal, which lost about 8 % THF-soluble materials, gave a spectrum similar to that of the raw coal in terms of the aromaticity and functionality (see below). Integration of the spectra gives only a slightly higher aromaticity (fa) value for the THF-extracted coal than for the raw coal. It should be noted that for some coals, the THF-extracted samples may display substantially different spectra. In addition, a general observation is that these NMR spectra are relatively poorly resolved, as compared to the spectra of pure materials, primarily because of the presence of a large number of different molecular species that have only slightly different chemical shifts.

Figure 2 shows the total ion chromatogram (TIC) obtained from Py-GC-MS of the THF-extracted raw coal. With the aid of computer-based data processing, it is now possible to perform a compound type analysis of coal pyrolysis products by using the selective ion monitoring technique in Py-GC-MS, as has been used for hydrocarbon type analysis of liquid fuels by GC-MS [22]. Low rank coals are known to have higher oxygen funtionalities [23], and therefore we have examined the oxygen compounds in the pyrolysis products by using the characteristic ion masses for phenol (m/z 94), cresol (m/z 108), xylenol (m/z 122), and catechol (m/z 110). Figure 3 shows the total ion chromatogram (TIC) and selected ion chrmatograms (SIC) in the extended retention time (RT) region of 2-22 min, which is a part of Figure 2. Within this range, the four most predominant peaks in the TIC are all phenollic compounds. Also found in this sample are catechol and methylcatechol. The two relatively large peaks around RT of 3 min are p- and o-xylene, in that order. It should be noted that there are a number of major hydrocarbon peaks which appeared between 0 to 2 min (Figure 2) and whose intensities are higher than the largest peak phenol in Figure 3. Those peaks are C_5-C_8 alkanes plus

alkenes, which are not well separated, and toluene, the second largest peak. There are many other small peaks appeared over the whole RT region, and selective ion monitoring at m/z 71 indicates that they are long-chain alkanes and alkenes. Overall, these results show that the DECS-9 coal contains significant amounts of oxygen-containing structural units such as phenol and alkylphenols as well as alkylbenzenes. It is also interesting to note that the long-chain aliphatics still exist after long time Soxhlet extraction with toluene and THF.

Characterization of Liquefaction Residues

CPMAS ^{13}C NMR

The temperature-programmed liquefaction (TPL) of DECS-9 Montana subbituminous coal was carried out at final temperature ranging from 300 to 425°C. Detailed discussion of the TPL may be found elsewhere [21]. For the sake of comparing the amount of organic materials in the THF-insoluble residues, Figure 4 shows the yields of THF- and toluene-soluble products plus gas from duplicate runs of Montana coal, as a function of final TPL temperature.

Figure 5 presents the NMR spectra. The spectrum of THF-extracted unreacted coal serves as a baseline. The THF-insoluble residue from TPL at final temperature of 300°C has a spectrum (Figure 5B) similar to that of the THF-extracted coal (Figure 5A). In this spectrum, an intense peak is present for aliphatic carbons (0-60 ppm) which may also include trace amounts of aliphatic ether (-C-O-X). This aliphatic peak becomes progressively smaller with increasing severity of liquefaction. The aromatic region has three peaks: an intense peak around 130 ppm (aromatic C), and two shoulders, one at about 142 ppm (possibly catechol-like C), and another at 152 ppm (phenolic or aromatic ether C). A peak at 181 ppm (carboxyl C), and a broad band around 212 ppm (ketone or aldehyde C) define the rest of the spectrum. The peaks at 142 and 212 ppm almost disappear after TPL at 350°C, and the peak at 181 also diminishes after TPL at 375°C. A decrease in intensity of the peak at 152 ppm is only observed after 375°C, and this is accompanied by further loss in aliphatic carbons. Concomitant with the decrease in total aliphatic carbons, the relative contribution from methyl carbons (0-25 ppm) increases. In general, the intensity of the aliphatic region (0-60 ppm) decreases, and the aromaticity increases with an increase in severity of TPL. Integration of the ^{13}C NMR spectra shown in Figure 5 indicates a progress increase in carbon aromaticity of the remaining organic materials in the residue. We are currently exploring the ways to quantitaively calculate the contents of different carbons both in the aromatic and aliphatic regions, and their changes with the TPL temperature by using the curve-fitting methods with the aid of computer-software.

Pyrolysis-GC-MS

Figure 5 shows the selected retention time region of 2-22 minutes of the Py-GC-MS chromatograms of the THF-extracted raw coal (A) and the residue from TPL at 300°C, the major peaks in which are identified in Table 1. Phenol, alkyl phenols, alkylbenzenes, catechols as well as alkanes and alkenes are formed from flash pyrolysis of the THF-extracted raw coal. Relative to this sample, there is apparent change in Py-GC-MS profile of the residue from TPL at 300°C. The appearance of a major peak for naphthalene and disappearance of catechol differentiate the latter from the former. This is especially interesting, since the NMR spectra of these two samples (Figure 4) and the corresponding yields of THF-solubles (7-9%) are similar to each other. From these results, it is clear that the reaction at 300°C did cause some structural change. The naphthalene peak in Figure 3 is due mainly to the use of tetralin solvent, because this peak was found to be very small with other solvent or without solvent. Since the residue has been extracted by THF for over 24 h, washed by acetone and pentane (to remove THF completely) and dried in vacuum at 90-100°C for 6 h, the naphthalene/tetralin remained in the residue must be either chemically bound to other species or physically entrapped in solvent-inaccessible micropores or closed pores which can not be removed by solvent extraction.

Also, it appeared that Py-GC-MS can detect some subtle differences in coal structure which are not easily detectable by CPMAS NMR. Combination of the NMR and Py-GC-MS data suggests that the original coal contains considerable quantities of catechol-like structures, which seem to disappear in the liquefaction residues above 300°C, and carboxyl groups, which almost disappear after 350°C, and also phenolic structures which diminish in concentration with increasing temperature. The analytical results point to the progressive loss of oxygen functional groups and aliphatic species from the macromolecular network of the subbituminous coal during its depolymerization in tetralin under TPL conditions. The higher conversions in TPL runs (relative to the conventional runs in tetralin) suggest that the removal of carboxylic and catechol groups from the coal during the programmed heat-up ($\leq$ 350°C) in tetralin may have contributed to minimizing the retrogressive crosslinking at higher temperatures.

Low-rank coals are characterized by low aromaticities and high oxygen functionalities. It seems possible from comparative examination of the coal conversion data and spectroscopic data that the TPL conditions may facilitate the reduction of crosslinking reactions of the thermally sensitive groups such as oxygen-functional groups at low temperatures in H-donor. Further work on the quantitative evaluation of coal structural change during liquefaction is

now in progress.

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Table 1 Major identified peaks in Figure 6

No.	MW	Identified Compound
1	106	p-Xylene
2	106	o-Xylene
3	120	C3-benzene
4	120	C3-benzene
5	94	Phenol
6	108	o-Cresol
7	108	m- + p-Cresol
8	122	Dimethylphenol
9	122	Ethylphenol
10	128	Naphthalene
11	136	C3-phenol
12	110	Catechol
13	124	Methylcatechol
14	142	Methylnaphthalene
15	124	Methylcatechol

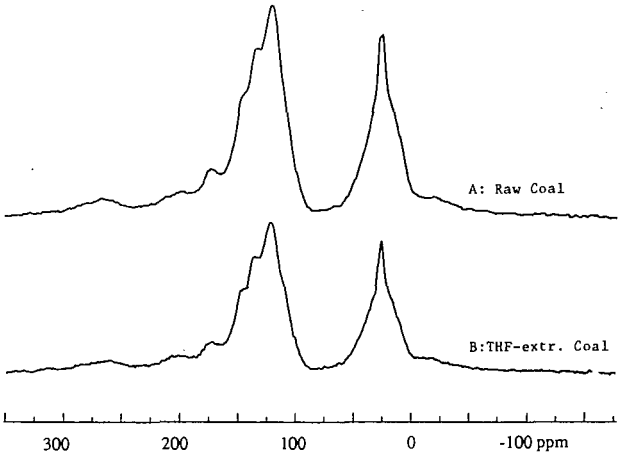

Figure 1 CPMAS ^{13}C NMR spectra of DECS-9 Montana subbituminous coal (A) and the THF-extracted coal (B).

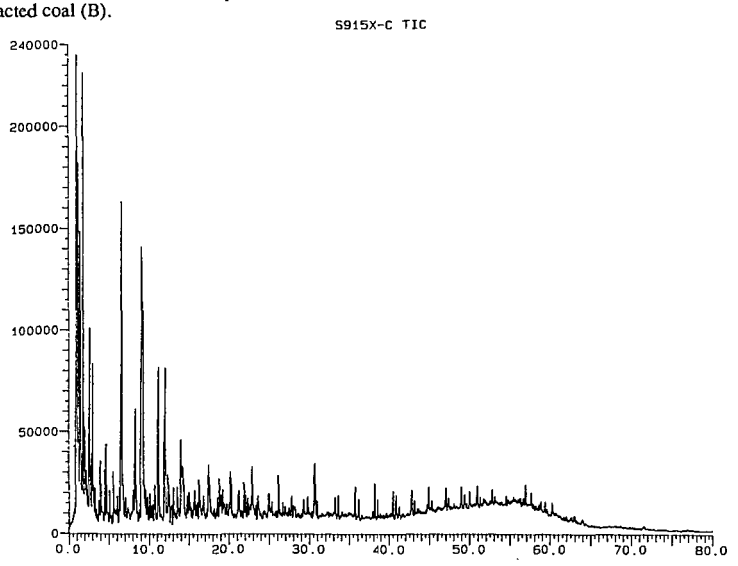

Figure 2 Totoal ion chromatogram for pyrolysis-GC-MS (610°C for 10 s) of THF-extracted DECS-9 Montana coal.

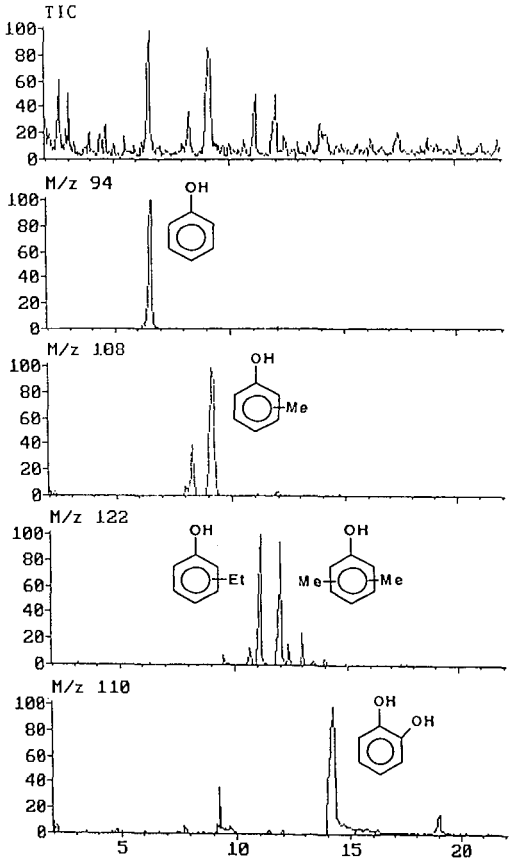

Figure 3 Specific ion chromatograms (SIC) and TIC from Py-GC-MS of THF-extracted, unreacted DECS-9 Montana subbituminous coal (pyrolysis at 610°C for 10 s)

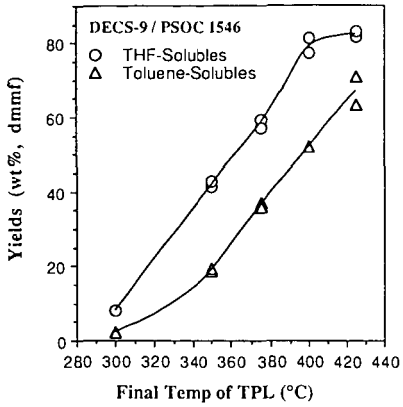

Figure 4 Conversion of DECS-9 Montana coal to THF- and toluene-solubles as a function of final temperature of temperature-programmed liquefaction (TPL) in tetralin.

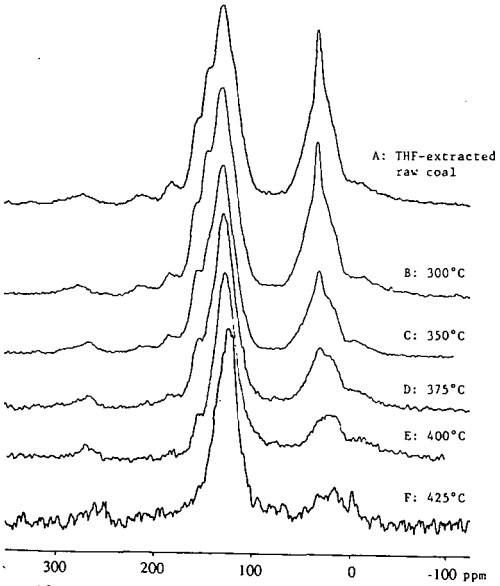

Figure 5 CPMAS ^{13}C NMR spectra of THF-insoluble residues from TPL of DECS-9 Montana coal in tetralin at different final temperature.

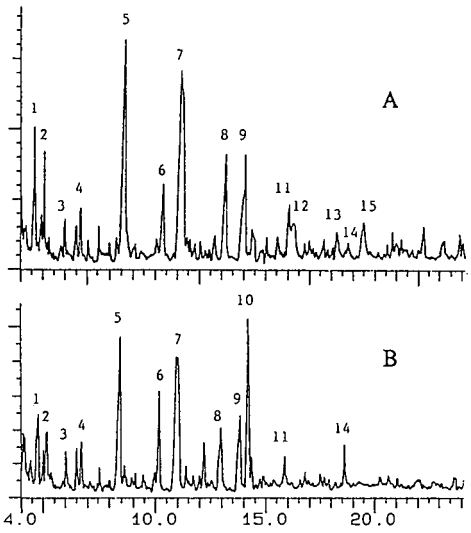

Figure 6 Py-GC-MS profiles of THF-extracted unreacted DECS-9 Montana subbituminous coal (A) and the residue (B) from TPL at final temperature of 300°C (pyrolysis at 610°C for 10 s).